

# A unified framework for dynamic density functional and Lattice Boltzmann methods

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(Dated: February 23, 2009)

## Abstract

Using methods of kinetic theory and liquid state theory we propose a description of the non-equilibrium behavior of molecular fluids which takes into account their microscopic structure and thermodynamic properties. The present work represents an alternative to the recent dynamic density functional theory which can only deal with colloidal fluids and is not apt to describe the hydrodynamic behavior of a molecular fluid. The method is based on a suitable modification of the Boltzmann transport equation for the phase space distribution and provides a detailed description of the local structure of the fluid and of the transport coefficients under inhomogeneous conditions. Finally, we propose a practical scheme to solve numerically and efficiently the resulting kinetic equation by employing a discretization procedure analogous to the one used in the Lattice Boltzmann method.

## I. INTRODUCTION

Understanding the dynamics of fluids under non-equilibrium conditions is of capital importance for fundamental statistical physics as well as applied disciplines such as engineering, fluid mechanics, rheology, and physiology. In recent years there has been an upsurge of interest towards the study of transport phenomena in strongly inhomogeneous systems mostly motivated by important physical and technological applications such as microfluidics<sup>1</sup>, colloids, oil recovery, lab-on-a-chip devices etc. These examples require the knowledge of structural and dynamical fluid properties in the presence of restricted geometries and/or structured substrates and of external gradients or time dependent fields. Typical time and length scales involved can be significantly shorter than those usually assumed in standard thermodynamic and hydrodynamic theories. In order to go beyond these descriptions, several theoretical approaches have been developed which differ not only by the nature of systems under scrutiny (colloidal systems have different dynamical behaviors in comparison with simple fluids), but also from subjective factors such as the individual scientific background and personal taste. These methods include the dynamic density functional approach, the kinetic approach, mesoscopic methods and methods based on effective free energies. In the present paper we shall be concerned in some detail only with the first two.

In the last thirty years, massive efforts have been devoted to develop techniques to study the properties of non-uniform interacting many particle systems, among these Density Functional theory (DFT) being perhaps the most versatile<sup>2,3</sup>. In DFT the single-particle density profile  $\rho(\mathbf{r})$  is obtained via minimization of the Grand potential functional. Functional derivatives of the Grand potential determine the multi-particle correlation functions and all the structural and thermodynamic properties for a system with arbitrary inhomogeneity. Recently, dynamical generalizations of these equilibrium methods have been applied to non-equilibrium problems such as diffusion, Stokes drift, polymeric fluids confined to cavities, etc. The dynamical density functional (DDF) is apt to describe the relaxation of Brownian particles in a medium and can be applied in situations where the local velocity distribution is very close to the Maxwellian and the density field varies slowly in time<sup>4,5</sup>. The method is based on the assumption of instantaneous equilibrium, i.e. that the correlation functions at

a given instant are identical to those of the same equilibrium system having the same equilibrium density profile. In the case of overdamped dynamics, which characterizes colloidal particles immersed in a solvent, the evolution is mainly governed by structural rearrangements so that such an interplay is evident and is justified to describe the evolution of the system in terms only of its density and density correlations. It is therefore not surprising that in DDF the velocity field is slaved to the density field and does not play any autonomous role.

On the other hand, in molecular fluids the momenta of the particles are not damped by the interaction with the solvent so that the total momentum is conserved and the momentum current must be treated on equal footing as the local density<sup>6,7</sup>. Hydrodynamics describes the non-equilibrium state of a system by means of a set of local variables which are density, momentum and temperature of the fluid<sup>8</sup>. However, hydrodynamics does not apply to phenomena which are not slowly varying in space and one has to consider a finer level of description, such as one based on a suitable generalization of the Boltzmann transport equation for  $f(\mathbf{r}, \mathbf{v}, t)$ , the phase space density distribution of particles with position  $\mathbf{r}$  and velocity  $\mathbf{v}$  at time  $t$ . The modeling of the interactions in the transport equation depends on the nature of the fluid and on the degree of accuracy required. The widely used Boltzmann collision operator has been studied for several kinds of interaction potentials and gives predictions for the transport coefficients, but does not provide an accurate representation of the thermodynamics and structural properties of fluids<sup>9,10,11,12</sup>. For simple applications one can even approximate further the interaction term by a linear relaxation term, as proposed by Bhatnagar, Gross and Krook (BGK)<sup>14</sup>. A more refined approximation is needed if one is interested in a dynamical description taking into account both the equilibrium properties of the fluid, such as the equation of state and the equilibrium density profile in an external force field, and the transport properties under inhomogeneous conditions. The Revised Enskog theory (RET), originally introduced by Van Beijeren and Ernst for hard sphere systems<sup>15</sup>, has the ability to describe the local fluid structure within a kinetic formalism. It can serve as a reference theory to study fluids with different types of interactions. However, even in the RET case a numerical solution is often too demanding in terms of computer speed and memory so that one has to resort to some simplifications. One of these has been proposed more than a decade ago by Dufty, Santos and Brey<sup>16</sup> and consists in separating the slowly evolving part of  $f(\mathbf{r}, \mathbf{v}, t)$ , associated with the five hydrodynamic modes, from the

fast non-hydrodynamic modes.

In the present work, we will show how to obtain a workable numerical method based on this equation which includes information about the microscopic nature of the fluid and contains hydrodynamics as a limiting case. This paper is organized as follows: In section II we introduce the transport equation and the collision operator, we define the hydrodynamic fields and derive the balance equations. In section III we briefly derive, for the sake of comparison, the DDF equation, in section IV we derive the equation of evolution for molecular fluids which differs from the DDF equation because it considers the evolution of the density, velocity and temperature fields altogether. In Sec. V, we propose to use the Lattice Boltzmann method as a strategy to solve numerically the transport equation. Finally, in Sec. VI we summarize and draw some conclusions.

## II. KINETIC THEORY

We consider a simple fluid, whose elementary constituents, the molecules, mutually interact via a pairwise, spherically symmetric potential  $U(r - r')$ . The statistical description of such a system is based on the exact BBGKY hierarchy of dynamical equations for the reduced distribution functions, whose first level is the following kinetic equation

$$\partial_t f(\mathbf{r}, \mathbf{v}, t) + \mathbf{v} \cdot \nabla f(\mathbf{r}, \mathbf{v}, t) + \frac{\mathbf{F}(\mathbf{r})}{m} \cdot \frac{\partial}{\partial \mathbf{v}} f(\mathbf{r}, \mathbf{v}, t) = \Omega(f|\mathbf{r}, \mathbf{v}, t) + B(f|\mathbf{r}, \mathbf{v}, t) \quad (1)$$

where  $f(\mathbf{r}, \mathbf{v}, t)$  is the one particle phase space density distribution at time  $t$  and at the point  $(\mathbf{r}, \mathbf{v})$ ,  $\mathbf{F}(\mathbf{r})$  is an external velocity-independent force field,  $\Omega(f|\mathbf{r}, \mathbf{v}, t)$  represents the effect on the single particle distribution function of the interactions among fluid particles and  $B(f|\mathbf{r}, \mathbf{v}, t)$  is a coupling to an external agent, usually termed heat-bath. The interaction term is given by the following exact expression

$$\Omega(\mathbf{r}, \mathbf{v}, t) = \frac{1}{m} \nabla_{\mathbf{v}} \int d\mathbf{r}' \int d\mathbf{v}' f_2(\mathbf{r}, \mathbf{v}, \mathbf{r}', \mathbf{v}', t) \nabla_{\mathbf{r}} U(|\mathbf{r} - \mathbf{r}'|) \quad (2)$$

involving the two particles distribution function,  $f_2(\mathbf{r}, \mathbf{v}, \mathbf{r}', \mathbf{v}', t)$ , which in turn depends on the three particle correlation function. However, in the simplest closure schemes  $\Omega(f)$  (and  $B(f)$ ) can be expressed in terms only of  $f(\mathbf{r}, \mathbf{v}, t)$  so that (1) becomes self-consistent and one can devise practical schemes of solution.

In order to avoid the difficult calculation of the two-particle distribution function, one can introduce an approximate truncation of the BBGKY hierarchy. That is, we assume the following factorization of  $f_2$

$$f_2(\mathbf{r}, \mathbf{v}, \mathbf{r}', \mathbf{v}', t) = f(\mathbf{r}, \mathbf{v}, t) f(\mathbf{r}', \mathbf{v}', t) g_2(\mathbf{r}, \mathbf{r}', t | n) \quad (3)$$

where  $g_2$  is the equilibrium static pair correlation function, a functional of the local density.

One can further coarse grain the description and use the kinetic equation (1) to derive, by the usual Chapman-Enskog method, the macroscopic hydrodynamic equations, where a limited set,  $(d+2)$ , fields, namely density, momentum current and energy density are assumed to represent the state of the fluid. To achieve this goal and obtain an autonomous set of equations by relating the currents of the hydrodynamics fields to the gradients of these fields, one needs to find first the form of the distribution  $f(\mathbf{r}, \mathbf{v}, t)$  when the system is perturbed from equilibrium. Having the perturbed form of  $f(\mathbf{r}, \mathbf{v}, t)$ , one can compute the transport coefficients and thus relate currents and fields, without assuming the phenomenological constitutive relations. The transport coefficients are usually studied under conditions of almost uniform density, so that the spatial dependence of  $f(\mathbf{r}, \mathbf{v}, t)$  can be taken into account only at linear order. However, under many circumstances the presence of density gradients strongly influences the thermodynamic and dynamical properties of a fluid so that it seems important to study the interplay between structure and dynamics.

### A. Hydrodynamic fields and balance equations

A direct solution of eq. (1) in terms of the unknown  $f(\mathbf{r}, \mathbf{v}, t)$  is clearly beyond reach. We thus follow a different strategy, originally proposed by Dufty, Santos and Brey in a study of the hard-sphere system. Their approximation is tantamount to treat separately and accurately the part of  $\Omega(f)$  contributing to the evolution equations for the hydrodynamic fields from the part relative to the non-hydrodynamic moments of the distribution, which can be safely approximated by a simple relaxation time ansatz.

A convenient way to analyze eq. (1) is to consider the equation for the lowest velocity moments of the distribution function, which correspond to the standard five hydrodynamic fields describing the slowly evolving part of  $f(\mathbf{r}, \mathbf{v}, t)$ . We first introduce the average local

density

$$n(\mathbf{r}, t) = \int d\mathbf{v} f(\mathbf{r}, \mathbf{v}, t), \quad (4)$$

the average local fluid velocity

$$\mathbf{u}(\mathbf{r}, t) = \frac{1}{n(\mathbf{r}, t)} \int d\mathbf{v} \mathbf{v} f(\mathbf{r}, \mathbf{v}, t) \quad (5)$$

and the average local temperature

$$T(\mathbf{r}, t) = \frac{m}{3k_B n(\mathbf{r}, t)} \int d\mathbf{v} (\mathbf{v} - \mathbf{u})^2 f(\mathbf{r}, \mathbf{v}, t) \quad (6)$$

where  $k_B$  is the Boltzmann constant. We shall employ throughout the paper the Einstein summation convention that repeated indices are implicitly summed over and the notation  $\partial_i$  to indicate the partial derivative w.r.t. the  $i$ -th cartesian component of the vector  $\mathbf{r}$  and  $\partial_t$  to indicate the partial derivative w.r.t. time.

A set of balance equations are obtained for density and momentum by multiplying both sides of eq. (1) by 1, and  $\mathbf{v}$ , respectively, and integrating w.r.t. velocity

$$\partial_t n(\mathbf{r}, t) + \partial_i (n(\mathbf{r}, t) u_i(\mathbf{r}, t)) = 0 \quad (7)$$

and

$$mn(\mathbf{r}, t) [\partial_t u_j(\mathbf{r}, t) + u_i(\mathbf{r}, t) \partial_i u_j(\mathbf{r}, t)] + \partial_i P_{ij}^{(K)}(\mathbf{r}, t) - F_j(\mathbf{r}) n(\mathbf{r}, t) - C_j^{(1)}(\mathbf{r}, t) = b_j^{(1)}(\mathbf{r}, t) \quad (8)$$

An analogous balance equation for the temperature field can be derived by multiplying (1) by  $m(\mathbf{v} - \mathbf{u})^2/2$  and integrating w.r.t.  $\mathbf{v}$

$$\frac{3}{2} n(\mathbf{r}, t) [\partial_t T(\mathbf{r}, t) + u_i(\mathbf{r}, t) \partial_i T(\mathbf{r}, t)] + P_{ij}^{(K)}(\mathbf{r}, t) \partial_i u_j(\mathbf{r}, t) + \partial_i q_i^{(K)}(\mathbf{r}, t) - C^{(2)}(\mathbf{r}, t) = b^{(2)}(\mathbf{r}, t) \quad (9)$$

To establish the momentum and temperature equations (8) and (9) we introduced some quantities, which in general cannot be expressed in terms of the hydrodynamic fields. These are the kinetic components of the pressure tensor, indicated with the superscript "K",

$$P_{ij}^{(K)}(\mathbf{r}, t) = m \int d\mathbf{v} f(\mathbf{r}, \mathbf{v}, t) (v - u)_i (v - u)_j \quad (10)$$

and the kinetic components of the heat flux vector

$$q_i^{(K)}(\mathbf{r}, t) = \frac{m}{2} \int d\mathbf{v} f(\mathbf{r}, \mathbf{v}, t) (\mathbf{v} - \mathbf{u})^2 (v - u)_i \quad (11)$$

In addition, we defined two terms stemming from molecular interactions (recall that  $\int \Omega d\mathbf{v} = 0$  and  $\int B d\mathbf{v} = 0$ , because the number of particles is conserved)

$$C_i^{(1)}(\mathbf{r}, t) = m \int d\mathbf{v} (v - u)_i \Omega(f|\mathbf{r}, \mathbf{v}, t). \quad (12)$$

and

$$C^{(2)}(\mathbf{r}, t) = \frac{m}{2} \int d\mathbf{v} (\mathbf{v} - \mathbf{u})^2 \Omega(f|\mathbf{r}, \mathbf{v}, t) \quad (13)$$

and two terms stemming from the coupling with the heat bath

$$b_i^{(1)}(\mathbf{r}, t) = m \int d\mathbf{v} (v - u)_i B(f|\mathbf{r}, \mathbf{v}, t). \quad (14)$$

and

$$b^{(2)}(\mathbf{r}, t) = \frac{m}{2} \int d\mathbf{v} (\mathbf{v} - \mathbf{u})^2 B(f|\mathbf{r}, \mathbf{v}, t) \quad (15)$$

Following ref.<sup>11</sup> one can relate the term  $C_i^{(1)}$  with the excess part of the pressure tensor,  $P_{ij}^{(C)}(\mathbf{r}, t)$ , stemming from the interactions,

$$C_i^{(1)}(\mathbf{r}, t) = -\partial_j P_{ij}^{(C)}(\mathbf{r}, t), \quad (16)$$

where the components of the excess part (over the ideal gas) of the pressure tensor can be computed using a method due to Irving and Kirkwood which gives the following exact expression

$$P_{ij}^{(C)}(\mathbf{r}, t) = -\frac{1}{2} \int_0^1 d\lambda \int d\mathbf{r}_{12} \int d\mathbf{v} d\mathbf{v}' \frac{\mathbf{r}_{12} \mathbf{r}_{12}}{|\mathbf{r}_{12}|} \frac{dU(|\mathbf{r}_{12}|)}{d|\mathbf{r}_{12}|} f_2(\mathbf{r} + (1-\lambda)\mathbf{r}_{12}, \mathbf{v}, \mathbf{r} - \lambda\mathbf{r}_{12}, \mathbf{v}', t) \quad (17)$$

with  $\mathbf{r}_{12} = (\mathbf{r} - \mathbf{r}')$ . With such an identification, eq. (8) assumes the form of the standard macroscopic equation for momentum balance. In general, no analogous relation exists between  $C^{(2)}(\mathbf{r}, t)$  and the excess component of the heat flux, and one should instead take into account also the transfer of potential energy in order to derive an expression in terms of macroscopic fluxes.

### III. COLLOIDAL DYNAMICS AND DENSITY FUNCTIONAL STRATEGY

Let us go back to the non-equilibrium case. Equation (1) contains as limiting cases the Hamiltonian dynamics and the fully underdamped dynamics when the heat bath exerts a large friction on the particles. In the standard description of the behavior of colloids it is

assumed that the particles are subject to two kinds of forces from the surrounding fluid 1) a deterministic friction, proportional to their velocity and described by Stokes law and 2) a stochastic force, characterized by a white noise spectrum, resulting from the interactions with the solvent molecules. In formulas, each particle is subjected to the following combination of solvent forces  $-m\gamma\mathbf{v} + \sqrt{2\gamma mk_B T}\xi$ , where  $\xi$  is a Gaussian white noise and  $\gamma$  a friction coefficient. A fluctuation-dissipation relation has been assumed between the noise amplitude and the friction coefficient so that the steady state velocity distribution is Maxwellian<sup>17</sup>. The effect of these forces on the particle phase space distribution  $f(\mathbf{r}, \mathbf{v}, t)$  can be represented by the following term in eq. (1)<sup>21</sup>

$$B^{(coll)}(f|\mathbf{r}, \mathbf{v}, t) = \gamma \left[ \frac{k_B T}{m} \frac{\partial^2}{\partial \mathbf{v}^2} + \frac{\partial}{\partial \mathbf{v}} \cdot \mathbf{v} \right] f(\mathbf{r}, \mathbf{v}, t) \quad (18)$$

Using the specific form of the heat-bath term, eq. (18), we shall now recover the dynamic density functional equation. In this case  $b_i^{(1)}(\mathbf{r}, t) = -m\gamma n(\mathbf{r}, t)u_i(\mathbf{r}, t)$ . The reduction of eq. (1) to a DDF dynamics can be done systematically by employing a multiple time scale approach, as used by Marconi and Tarazona<sup>18,19,20</sup>. The method eliminates systematically all high moments of the velocity distribution function except the zeroth moment, that is the number density, by employing an asymptotic expansion in the inverse friction parameter  $\gamma^{-1}$ . The result is an equation for the density field containing corrections to the standard non-linear diffusion equation usually employed in DDF. However, for the present scope, we shall employ an heuristic and much simpler method to contract the phase space description of eq. (1) into the DDF description.

We start by considering an approximate solution of the transport equation of the form

$$f_{DDF}(\mathbf{r}, \mathbf{v}, t) = n(\mathbf{r}, t) \left[ 1 + \frac{\mathbf{v} \cdot \mathbf{u}(\mathbf{r}, t)}{v_T^2} \right] \phi_0(\mathbf{v}) \quad (19)$$

with  $\phi_0(\mathbf{v}) = \left[ \frac{1}{2\pi v_T^2} \right]^{3/2} \exp\left(-\frac{m\mathbf{v}^2}{2v_T^2}\right)$  and  $v_T^2 = k_B T/m$ . Substituting eq. (19) into (1)

$$\begin{aligned} & \phi_0(\mathbf{v}) \{ [\partial_t n(\mathbf{r}, t) + \partial_i(n(\mathbf{r}, t)u_i(\mathbf{r}, t))] + \\ & \frac{v_i}{v_T^2} [\partial_t(n(\mathbf{r}, t)u_i(\mathbf{r}, t)) + v_T^2 \partial_i n(\mathbf{r}, t) - \frac{F_i}{m} n(\mathbf{r}, t) + \gamma n(\mathbf{r}, t)u_i(\mathbf{r}, t)] + \\ & \left( \frac{v_j v_j}{v_T^2} - \delta_{ij} \right) [\partial_i(u_j(\mathbf{r}, t)n(\mathbf{r}, t)) - \frac{F_i}{m} u_i(\mathbf{r}, t)n(\mathbf{r}, t)] \} = \Omega(\mathbf{r}, \mathbf{v}, t) \end{aligned} \quad (20)$$

Multiplying by 1 and by  $v_i$  eq.(20) and integrating w.r.t. velocity, we obtain the continuity equation (7) and the following equation for the momentum current

$$m\partial_t(n(\mathbf{r}, t)u_i(\mathbf{r}, t)) + \gamma m n(\mathbf{r}, t)u_j(\mathbf{r}, t) + k_B T \partial_i n(\mathbf{r}, t)(\mathbf{r}, t) - F_i(\mathbf{r})n(\mathbf{r}, t) - C_i^{(1)}(\mathbf{r}, t) = 0, \quad (21)$$



The DDF equation is recovered if one takes  $\gamma$  large and neglects the time derivative of the momentum current,  $n(\mathbf{r}, t)u_i(\mathbf{r}, t)$ ), viz. one neglects the time derivative in the l.h.s of eq. (21). Using the continuity equation (7) to eliminate the current one obtains the following diffusion equation

$$\partial_t n(\mathbf{r}, t) = \frac{1}{m\gamma} \partial_i [k_B T \partial_i n(\mathbf{r}, t) - F_i(\mathbf{r}) n(\mathbf{r}, t) - C_i^{(1)}(\mathbf{r}, t)] \quad (22)$$

In order to identify the full DDF equation one must specify the form of the collision term  $C_i^{(1)}(\mathbf{r}, t)$ .

We begin by a simple ansatz for the interaction term (2) by assuming the following adiabatic approximation

$$\Omega_{DDF}(\mathbf{r}, \mathbf{v}, t) = \frac{1}{m} \frac{\partial}{\partial v_i} \int d\mathbf{r}' \int d\mathbf{v}' f(\mathbf{r}, \mathbf{v}, t) f(\mathbf{r}', \mathbf{v}', t) g_2(\mathbf{r}, \mathbf{r}', t|n) \frac{\partial}{\partial r_i} U(|\mathbf{r} - \mathbf{r}'|) \quad (23)$$

where we have approximated the two-particle correlations by those of an equilibrium system having the same density profile as the system at time  $t$ . Next, we define the molecular field as

$$F_i^{(mol)}(\mathbf{r}, t) = - \int d\mathbf{r}' n(\mathbf{r}', t) g_2(\mathbf{r}, \mathbf{r}', t|n) \frac{\partial}{\partial r_i} U(|\mathbf{r} - \mathbf{r}'|) \quad (24)$$

so that the interaction term becomes

$$\Omega_{DDF}(\mathbf{r}, \mathbf{v}, t) = - \frac{1}{m} \frac{\partial}{\partial v_i} f(\mathbf{r}, \mathbf{v}, t) F_i^{(mol)}(\mathbf{r}, t) \quad (25)$$

By computing the corresponding  $C_i^{(1)}$  from (12) the result is

$$C_i^{(1)}(\mathbf{r}, t) = n(\mathbf{r}, t) F_i^{(mol)}(\mathbf{r}, t). \quad (26)$$

It is straightforward to show that expression (26) can be recast as

$$C_i^{(1)}(\mathbf{r}, t) = -n(\mathbf{r}, t) \frac{\partial}{\partial r_i} \frac{\delta \Delta \mathcal{F}}{\delta n(\mathbf{r}, t)} \quad (27)$$

where  $\Delta \mathcal{F}$  is the free energy excess over the ideal gas<sup>4</sup>.

Notice that, in the case treated above, both the noise and the friction are externally imposed by the presence of the solvent and such an heat bath term breaks the translational invariance of the system, since the heat bath is assumed to be at rest.

Unfortunately, as shown in ref.<sup>18</sup>, the method cannot be extended to systems with small or vanishing friction proportional to the velocity and therefore cannot be extended to describe

dense liquids, which are instead characterized by an internal friction proportional to velocity gradients and not to the velocity itself. The slaving of the momentum current and of the energy current to the density, which allows the reduction of the complex dynamics eq. (1) to eq. (22) is at work only in the high friction regime. Hence, a different approach is needed to treat molecular fluids.

#### IV. MOLECULAR FLUIDS AND MODIFIED BOLTZMANN EQUATION STRATEGY

The dynamics of molecular fluids is described by Newton's equation of motion, as opposed to colloidal fluids where the presence of the solvent corresponds to overdamped Brownian dynamics encapsulated in the DDF equation. Two important properties of molecular fluids must be preserved in any theoretical representation. These are the Galilei invariance, with respect to the reference frames moving relative to each other at constant velocity, and the momentum conservation. These are relevant features of hydrodynamics and are not displayed by the DDF method, where the absolute velocities are damped, thus privileging the "solvent reference frame". In the case of molecular fluids, the total momentum must be conserved, so that a heat bath such as that used in the previous section is not acceptable. In a molecular fluid the dissipation is determined by other mechanisms such as, among the others, the internal friction proportional to velocity gradients (viscosity), and not to velocity itself, and to temperature gradients (thermal conductivity). We shall use this information in order to make approximations not violating these conservation laws, which are at the origin of the low frequency hydrodynamic modes.

We start by splitting  $\Omega$  into two contributions, the first taking into account accurately the effect of the interaction term on the hydrodynamic variables, so that a correct thermodynamic and structure of the fluid is achieved, and the second describing in lesser detail the evolution of the non-hydrodynamic modes.

Based on the form of eqs.(4), (5) and (6), we write

$$\Omega(f|\mathbf{r}, \mathbf{v}, t) = \frac{\phi_M(\mathbf{r}, \mathbf{v}, t)}{k_B T(\mathbf{r}, t)} \left( (\mathbf{v} - \mathbf{u}) \cdot \mathbf{C}^{(1)}(\mathbf{r}, t) + \left( \frac{m(\mathbf{v} - \mathbf{u})^2}{3k_B T(\mathbf{r}, t)} - 1 \right) C^{(2)}(\mathbf{r}, t) \right) + \delta\Omega(f|\mathbf{r}, \mathbf{v}, t) \quad (28)$$

with

$$\phi_M(\mathbf{r}, \mathbf{v}, t) = \left[ \frac{m}{2\pi k_B T(\mathbf{r}, t)} \right]^{3/2} \exp \left( -\frac{m(\mathbf{v} - \mathbf{u})^2}{2k_B T(\mathbf{r}, t)} \right). \quad (29)$$

Equation (28) represents a separation of the interaction term  $\Omega(f)$  into a direct contribution to the hydrodynamic modes, plus a correction,  $\delta\Omega$ , which is assumed not to act directly on these modes. It is easy to see that the following approximation for the term  $\delta\Omega$  fulfills such a condition

$$\delta\Omega(f|\mathbf{r}, \mathbf{v}, t) \simeq \nu_0 \left[ \frac{k_B T(\mathbf{r}, t)}{m} \frac{\partial^2}{\partial \mathbf{v}^2} + \frac{\partial}{\partial \mathbf{v}} \cdot (\mathbf{v} - \mathbf{u}(\mathbf{r}, t)) \right] f(\mathbf{r}, \mathbf{v}, t) \quad (30)$$

In fact, by direct inspection one sees that the form of  $\Omega(f)$  eq.(28) together with eq.(30) reproduces eqs. (12) and (13), and that  $\delta\Omega$  does not contribute to these two integrals. The term  $\delta\Omega$  is assumed to be linear with respect to  $f$  and is approximated by an heat-bath operator. At variance with the heat bath operator introduced in the colloidal problem, its effect is to induce a matching of the velocity of the particles to the local value of the average velocity of the fluid and a matching of the temperature of the particles to the local value of the average temperature. The coefficient  $\nu_0$  is a phenomenological adjustable parameter chosen to reproduce the value of the viscosity of the fluid. The simplified and approximated version of (1) represented by eq. (28) with eq. (30) reproduces by construction equations (7), (8) and (9). We comment that the form (30) preserves the Galilei invariance of the fluid. This heat bath “co-moving” with the fluid is of course very different from the one introduced in the study of colloids. Physically it can be thought to represent the effect of the fast modes on the slow modes, and can be seen as an intrinsic heat bath, as opposed to the extrinsic heat bath employed in the study of colloids.

We remark that the invariance of the heat bath with respect to the choice of the reference frame is the same requirement which has lead to the formulation of the so-called Dissipative Particle Dynamics (DPD)<sup>22,23</sup>. There on a phenomenological basis one introduces pairwise dissipative and random forces, a “DPD thermostat” which locally conserves the momentum and leads the emergence of hydrodynamic flow effects on the macroscopic scale<sup>24</sup>. The present method instead of introducing a pairwise friction proportional to the velocity difference of two colliding particles, employs a frictional force proportional to the difference between the individual particle velocity and the average fluid velocity  $\mathbf{u}$ .

It is useful to represent  $f(\mathbf{r}, \mathbf{v}, t)$  as the sum of a local thermodynamic equilibrium state,  $f_{loc}(\mathbf{r}, \mathbf{v}, t) = n(\mathbf{r}, t)\phi_M(\mathbf{r}, \mathbf{v}, t)$ , plus a contribution representing the deviation from such a state

$$f(\mathbf{r}, \mathbf{v}, t) = f_{loc}(\mathbf{r}, \mathbf{v}, t) + \delta f(\mathbf{r}, \mathbf{v}, t) \quad (31)$$

The function  $f_{loc}(\mathbf{r}, \mathbf{v}, t)$  alone fully determines the values of the hydrodynamic moments (4), (5) and (6), whereas  $\delta f(\mathbf{r}, \mathbf{v}, t)$  does not contribute. On the other hand,  $\delta f$  does contribute to the heat flux and to the viscous pressure tensor as shown below. The interplay between  $\delta f$  and the hydrodynamic fields occurs both via the terms  $C^{(1)}$  and  $C^{(2)}$ , which are functionals of  $\delta f$  and  $f_{loc}$  and via kinetic components of the pressure tensor and heat flux vector.

It is relevant to remark that  $\delta\Omega$  vanishes when  $f = f_{loc}$ . The mathematical properties of the differential operator featuring in eq. (30) are well-known, in particular displaying a non-positive spectrum with discrete eigenvalues  $0, -\nu_0, -2\nu_0, \dots$ . The local Maxwellian (29) represents the eigenfunction associated with the null eigenvalue, whereas the higher-order eigenfunctions are associated with the non hydrodynamic modes. However, for practical purposes it is more convenient to simplify further this term and resort to a drastic assumption, by replacing the heat bath term (30) by a BGK-like relaxation term

$$\delta\Omega(f|\mathbf{r}, \mathbf{v}, t) = -\nu_0 \left( f(\mathbf{r}, \mathbf{v}, t) - n(\mathbf{r}, t)\phi_M(\mathbf{r}, \mathbf{v}, t) \right) = -\nu_0 \delta f(\mathbf{r}, \mathbf{v}, t) \quad (32)$$

which keeps the relevant properties of (30), at the price of assuming a single relaxation time,  $\nu_0^{-1}$ , for all non-hydrodynamic modes.

Here,  $\nu_0$  is a phenomenological parameter, representing a collision frequency, chosen as to reproduce the viscosity of the fluid. The above approximation replaces by a much simpler relaxation the complicated effects of the interactions among the non-hydrodynamic moments. The action of  $\delta\Omega$  is to induce a rather fast relaxation of the solution towards a state of local equilibrium<sup>25</sup>. Once such a state has been reached the system evolves towards the steady state via equilibration of different regions through exchange of hydrodynamic fluxes.

In addition, since also the term enforcing the local equilibrium condition (30) contains as local parameters  $\mathbf{u}(\mathbf{r}, t)$  and  $T(\mathbf{r}, t)$ , the system has the correct long wavelength properties required by hydrodynamics. For future reference we rewrite the combination of eq.(1), (28) and (32)

$$\begin{aligned} \partial_t f(\mathbf{r}, \mathbf{v}, t) + \mathbf{v} \cdot \nabla f(\mathbf{r}, \mathbf{v}, t) + \frac{\mathbf{F}^{ext}(\mathbf{r})}{m} \cdot \frac{\partial}{\partial \mathbf{v}} f(\mathbf{r}, \mathbf{v}, t) - \\ \frac{\phi_M(\mathbf{r}, \mathbf{v}, t)}{k_B T(\mathbf{r}, t)} \left( (\mathbf{v} - \mathbf{u}) \cdot \mathbf{C}^{(1)}(\mathbf{r}, t) + \left( \frac{m(\mathbf{v} - \mathbf{u})^2}{3k_B T(\mathbf{r}, t)} - 1 \right) C^{(2)}(\mathbf{r}, t) \right) = -\nu_0 \delta f(\mathbf{r}, \mathbf{v}, t) \end{aligned} \quad (33)$$

The advantage of using eq. (33) instead of the apparently equivalent set of coupled hydrodynamic equations is the following. Even in the non-interacting case the moments of the distribution function are coupled and to interrupt the hierarchy one needs a truncation

scheme. This truncation can be avoided by working directly with eq. (33), where one can apply the powerful technique of the Lattice Boltzmann equation (LBE). In the LBE one discretizes the velocity and the coordinates of the particles using a finite grid and computes directly the distribution function  $f(\mathbf{r}, \mathbf{v}, t)$ . This program would have been numerically too demanding if we had to use eq. (1) because of the large number of integrals involved in the evaluation of the interaction term.

Eq. (33) treats the hydrodynamic moments in a privileged fashion and describes a rapid equilibration of the system toward the local equilibrium state. The remaining stage is described by hydrodynamics, that is by mass, momentum and energy transport on larger scales.

### A. Approximate solution, kinetic contribution to the viscosity and heat conduction

Although this procedure is not necessary in numerical work, in order to gain some insight, in the present section we shall determine  $\delta f$  perturbatively starting from  $f_{loc}$ , the local equilibrium state. We substitute  $f \simeq f_{loc}$  in the l.h.s. of (33) and obtain an equation for  $\delta f$  in terms of derivatives of the hydrodynamic fields.

The details of the calculation can be found in standard textbooks<sup>26</sup> and hence will be skipped here. The substitution of  $f_{loc}$  in the left hand side of eq. (33) gives

$$\begin{aligned} & \left\{ [\partial_t n + \partial_i (n u_i)] + [n \partial_t u_k + n u_i \partial_i (n u_k) + \partial_k (n T) - \frac{F_k}{m} - C_k^{(1)}] \frac{m(v_k - u_k)}{k_B T} \right. \\ & + \frac{n}{2T} [\partial_t T + u_i \partial_i T + \frac{2}{3} T \partial_i u_i - \frac{2}{3n} C^{(2)}] \left( \frac{m(\mathbf{v} - \mathbf{u})^2}{k_B T} - 3 \right) + \frac{n}{T} \partial_i T \left( m \frac{(\mathbf{v} - \mathbf{u})^2}{2k_B T} - \frac{5}{2} \right) (v_i - u_i) \\ & \left. + m \frac{n}{k_B T} \left( (v_i - u_i)(v_k - u_k) - \frac{(\mathbf{v} - \mathbf{u})^2}{3} \delta_{ij} \right) \partial_i u_k \right\} \phi_M(\mathbf{r}, \mathbf{v}, t) = - \frac{\delta f(\mathbf{r}, \mathbf{v}, t)}{\nu_0} \end{aligned} \quad (34)$$

Since  $\delta f$  does not contain terms proportional to the first three terms of the above equation, because it must have vanishing hydrodynamic moments, we must impose that the first three terms in the l.h.s. vanish. These are the so-called solvability conditions and are precisely the balance equations (7), (8) and (9) at the Euler level, i.e. without kinetic viscosity and heat conduction contributions.

We thus obtain the following explicit representation of  $\delta f$

$$\begin{aligned} \delta f = & -\frac{1}{\nu_0} \frac{n(\mathbf{r}, t)}{T} \phi_M(\mathbf{r}, \mathbf{v}, t) \left[ \left( \frac{m}{2} \frac{(\mathbf{v} - \mathbf{u})^2}{k_B T(\mathbf{r}, t)} - \frac{5}{2} \right) (v_i - u_i) \partial_i T(\mathbf{r}, t) \right. \\ & \left. + m \left( (v_i - u_i)(v_k - u_k) - \frac{(\mathbf{v} - \mathbf{u})^2}{3} \delta_{ij} \right) \partial_i u_k(\mathbf{r}, t) \right]. \end{aligned} \quad (35)$$

The actual solution  $\delta f$ , which can be determined by solving numerically eq. (33) contains higher-order terms, but we shall not try to go beyond the approximation (35) in the present paper. Instead, we determine the kinetic contribution to the transport coefficients. We first compute the heat flux vector by substituting  $\delta f$  in eq.(11)

$$q_i(\mathbf{r}, t) = -\frac{5}{2} \frac{1}{m\nu_0} n(\mathbf{r}, t) k_B^2 T(\mathbf{r}, t) \partial_i T(\mathbf{r}, t) \quad (36)$$

and secondly we compute the components of the pressure tensor (10)

$$P_{ij}^{(K)}(\mathbf{r}, t) = k_B T(\mathbf{r}, t) n(\mathbf{r}, t) \delta_{ij} - \frac{1}{\nu_0} \frac{n(\mathbf{r}, t) k_B T(\mathbf{r}, t)}{m} \left( (\partial_i u_j(\mathbf{r}, t) + \partial_j u_i(\mathbf{r}, t)) - \frac{2}{3} \partial_k u_k(\mathbf{r}, t) \delta_{ij} \right) \quad (37)$$

By comparing (36) with the macroscopic expression  $q_i = -\lambda \partial_i T$  we obtain the kinetic contribution to the heat conductivity

$$\lambda^{(K)} = \frac{5}{2} \frac{1}{m\nu_0} n k_B^2 T \quad (38)$$

By comparing (37) with the macroscopic definition of pressure tensor,

$$P_{ij}^{(K)}(\mathbf{r}, t) = k_B T n \delta_{ij} - \left( \eta^{(K)} (\partial_i u_j + \partial_j u_i) + (\eta_b^{(K)} - \frac{2}{3} \eta^{(K)}) \partial_k u_k \delta_{ij} \right) \quad (39)$$

where  $\eta_b$  is the bulk viscosity coefficient, we find the kinetic contribution to the shear viscosity coefficient

$$\eta^{(K)} = \frac{n k_B T}{\nu_0} \quad (40)$$

and

$$\eta_b^{(K)} = 0 \quad (41)$$

It is important to stress that in the Euler approximation it is not possible to have a stationary solution because there is no dissipation mechanism to release the energy injected by an external force, so that viscosity and heat conduction are necessary. Finally, in order to make contact with the literature one can fix the free parameter of the theory,  $\nu_0$ , and choose  $\nu_0 = n \sigma^2 \sqrt{2 k_B T / m}$ , with  $\sigma$  the diameter of the equivalent hard sphere, and find  $\eta^{(K)} = \frac{k_B T m}{\sqrt{2}} \sigma^2$ .

## B. Short range repulsive potentials

To proceed further, one must solve eq. (33) and obtain explicit expressions for the thermodynamic fields and the transport coefficients. Thus, we need a specific form of the interaction potential  $U(r, r')$  and consequently of  $\Omega(\mathbf{r}, \mathbf{v}, t)$ . We shall relate the microscopic details to the transport coefficients so that we need to compute the quantities  $C_i^{(1)}$  and  $C^{(2)}$ .

The prototypical short range repulsive potential is represented by the hard sphere potential for which one has to consider a special treatment of the interaction term in order to obtain an accurate representation of the excess quantities. In particular, such an interaction can be treated as a collision process and the collisions as an uncorrelated binary sequence. A first approximation of  $\Omega[f](\mathbf{r}_1, \mathbf{v}, t)$  is given by the ‘‘Stosszahl ansatz’’ which renders (1) an equation involving only the single-particle distribution decoupled from higher-order distribution functions

$$\begin{aligned} \Omega_B[f](\mathbf{r}, \mathbf{v}, t) = & \sigma^2 \int d\mathbf{v}_2 \int d\hat{\mathbf{b}} \Theta(\hat{\mathbf{b}} \cdot \mathbf{v}_{12})(\hat{\mathbf{b}} \cdot \mathbf{v}_{12}) \times \\ & [f(\mathbf{r}, \mathbf{v}', t)f(\mathbf{r}, \mathbf{v}_2', t) - f(\mathbf{r}, \mathbf{v}, t)f(\mathbf{r}, \mathbf{v}_2, t)] \end{aligned} \quad (42)$$

where  $\mathbf{v}'$  and  $\mathbf{v}_2'$  are scattered velocities given by  $\mathbf{v}' = \mathbf{v} - (\hat{\mathbf{b}} \cdot \mathbf{v}_{12})\hat{\mathbf{b}}$  and  $\mathbf{v}_2' = \mathbf{v}_2 + (\hat{\mathbf{b}} \cdot \mathbf{v}_{12})\hat{\mathbf{b}}$  with  $\mathbf{v}_{12} = \mathbf{v} - \mathbf{v}_2$ .

At higher densities, however, the ‘‘Stosszahl ansatz’’ fails to describe both the structural and relaxational properties of the fluid because collision sequences become highly correlated. To include these sequences and extend the transport equation to higher densities in the Seventies van Beijeren and Ernst have developed the revised Enskog theory (RET), taking into account the effects of ternary and higher-order collisions and the difference in positions of two hard-spheres at collision. Such a feature allows the instantaneous transfer of momentum and energy during a collision. In particular this transport mechanism gives rise to non-ideal gas contributions to the pressure and to the heat flux, which were neglected in Boltzmann’s treatment of collisions. The RET collision operator takes the form

$$\begin{aligned} \Omega_{RET}[f](\mathbf{r}, \mathbf{v}, t) = & \sigma^2 \int d\mathbf{v}_2 \int d\hat{\mathbf{b}} \Theta(\hat{\mathbf{b}} \cdot \mathbf{v}_{12})(\hat{\mathbf{b}} \cdot \mathbf{v}_{12}) \times \\ & [g_2(\mathbf{r}, \mathbf{r} - \hat{\mathbf{b}}\hat{\mathbf{b}}, t|n)f(\mathbf{r}, \mathbf{v}', t)f(\mathbf{r} - \hat{\mathbf{b}}\hat{\mathbf{b}}, \mathbf{v}_2', t) \\ & - g_2(\mathbf{r}, \mathbf{r} + \hat{\mathbf{b}}\hat{\mathbf{b}}, t|n)f(\mathbf{r}, \mathbf{v}, t)f(\mathbf{r} + \hat{\mathbf{b}}\hat{\mathbf{b}}, \mathbf{v}_2, t)] \end{aligned} \quad (43)$$

In order to obtain an explicit representation of the excess pressure tensor and heat flux we must compute, as prescribed by (12) and (13), the integrals of  $\Omega_{RET}(\mathbf{r}, \mathbf{v}, t)$  times  $G_i^{(1)}(\mathbf{v}) =$

$m(v - u(\mathbf{r}, t))_i$  and  $G^{(2)}(\mathbf{v}) = \frac{m}{2}(\mathbf{v} - \mathbf{u}(\mathbf{r}, t))^2$ . After replacing  $(\mathbf{v}, \mathbf{v}_2, \hat{\mathbf{B}}) \rightarrow (\mathbf{v}', \mathbf{v}'_2, -\hat{\mathbf{B}})$ , the RET explicit form of eqs. (12,13) reads

$$C_{\underline{\alpha}}^{(l)}(\mathbf{r}, t) = \frac{\sigma^2}{2} \int d\mathbf{v} \int d\mathbf{v}_2 \int d\hat{\mathbf{B}} \Theta(\hat{\mathbf{B}} \cdot \mathbf{v}_{12})(\hat{\mathbf{B}} \cdot \mathbf{v}_{12}) [G_{\underline{\alpha}}^{(l)}(\mathbf{v}') - G_{\underline{\alpha}}^{(l)}(\mathbf{v})] \times \\ \left[ g_2(\mathbf{r}, \mathbf{r} + \hat{\mathbf{B}}, t|n) f(\mathbf{r}, \mathbf{v}, t) f(\mathbf{r} + \hat{\mathbf{B}}, \mathbf{v}_2, t) - g_2(\mathbf{r}, \mathbf{r} - \hat{\mathbf{B}}, t|n) f(\mathbf{r}, \mathbf{v}_2, t) f(\mathbf{r} - \hat{\mathbf{B}}, \mathbf{v}, t) \right] \quad (44)$$

In the case of the hard-sphere fluid, where there is no contribution to the internal energy stemming from the pair potential, one finds the simple relation

$$C_{HS}^{(2)}(\mathbf{r}, t) = -[\nabla_i q_i^{(C)}(\mathbf{r}, t) + P_{ij}^{(C)}(\mathbf{r}, t) \nabla_i \mathbf{u}_j(\mathbf{r}, t)], \quad (45)$$

where the first term represents the divergence of the heat flux and the second the contribution due to the viscous heating.

At this stage we simplify drastically the calculation of the interaction term and neglect the contribution  $\delta f(\mathbf{r}, \mathbf{v}, t)$  to the integrals (44). We assume  $f(\mathbf{r}, \mathbf{v}, t) = n(\mathbf{r}, t) \phi_M(\mathbf{r}, \mathbf{v}, t)$ , which depends on the three hydrodynamic fields  $n, u, T$ . Substituting now this approximation into (44) and expanding to first order  $\phi_M(\mathbf{r} \pm \hat{\mathbf{B}}, \mathbf{v}, t)$  about  $\mathbf{u}(\mathbf{r}, t)$  and  $T(\mathbf{r}, t)$

$$\phi_M(\mathbf{r} \pm \hat{\mathbf{B}}, \mathbf{v}, t) \simeq \left[ \frac{m}{2\pi k_B T(\mathbf{r}, t)} \right]^{3/2} \exp \left[ -\frac{m(\mathbf{v} - \mathbf{u}(\mathbf{r}, t))^2}{2k_B T(\mathbf{r}, t)} \right] \times \\ \left\{ 1 + \frac{m[\mathbf{v} - \mathbf{u}(\mathbf{r}, t)] \cdot [\mathbf{u}(\mathbf{r} \pm \hat{\mathbf{B}}) - \mathbf{u}(\mathbf{r})]}{k_B T(\mathbf{r}, t)} \right. \\ \left. + \frac{m[\mathbf{v} - \mathbf{u}(\mathbf{r}, t)] \cdot [\mathbf{v} - \mathbf{u}(\mathbf{r}, t)] - 3k_B T(\mathbf{r}, t)}{2k_B T^2(\mathbf{r}, t)} [T(\mathbf{r} \pm \hat{\mathbf{B}}, t) - T(\mathbf{r}, t)] + \dots \right\}$$

we arrive, after some lengthy algebra, to the result

$$C_i^{(1)}(\mathbf{r}, t) = -k_B T(\mathbf{r}, t) n(\mathbf{r}, t) \sigma^2 \int d\hat{\mathbf{B}} \hat{\mathbf{B}}_i g_2(\mathbf{r}, \mathbf{r} + \hat{\mathbf{B}}, t|n) n(\mathbf{r} + \hat{\mathbf{B}}, t) \\ \left[ 1 - \frac{2}{\sqrt{\pi k_B T(\mathbf{r}, t)/m}} \hat{\mathbf{B}} \cdot [\mathbf{u}(\mathbf{r} + \hat{\mathbf{B}}, t) - \mathbf{u}(\mathbf{r}, t)] + \frac{T(\mathbf{r} + \hat{\mathbf{B}}, t) - T(\mathbf{r}, t)}{2T(\mathbf{r}, t)} \right] \quad (46)$$

and

$$C^{(2)}(\mathbf{r}, t) = k_B T(\mathbf{r}, t) n(\mathbf{r}, t) \sigma^2 \int d\hat{\mathbf{B}} g_2(\mathbf{r}, \mathbf{r} + \hat{\mathbf{B}}, t|n) n(\mathbf{r} + \hat{\mathbf{B}}, t) \\ \left[ -\frac{\hat{\mathbf{B}} \cdot [\mathbf{u}(\mathbf{r} + \hat{\mathbf{B}}, t) - \mathbf{u}(\mathbf{r}, t)]}{2} + \frac{1}{\sqrt{\pi}} \sqrt{\frac{k_B T(\mathbf{r}, t)}{m}} \frac{T(\mathbf{r} + \hat{\mathbf{B}}, t) - T(\mathbf{r}, t)}{T(\mathbf{r}, t)} \right] \quad (47)$$



A comment is in order. In the hard-sphere fluid, momentum and energy fluxes can be transferred instantaneously even when the velocity distribution function has a Maxwellian form, provided it peaks at the local hydrodynamic velocity with a spread determined by the local temperature. As a consequence, we obtain a contribution not only to the pressure but also to the transport coefficients even within a Maxwellian approximation to the distribution function. This result is at variance with the corresponding result in the case of the Boltzmann equation where the collision term does not contribute neither to the pressure nor to the transport coefficients when the distribution is Maxwellian.

### C. Collisional contribution to the transport coefficients in the Hard-Sphere fluid

We now apply our method to compute the fluid transport coefficients in bulk conditions.

*Shear viscosity.* We assume both the density and the temperature to be uniform throughout the system, i.e.  $n(\mathbf{r}, t) = n_0$  and  $T(\mathbf{r}, t) = T_0$  whereas the velocity profiles varies along a direction normal to the stream lines

$$\mathbf{u} = (0, u_y(x, 0), 0) \quad (48)$$

We then use the equations

$$P_{xy} = P_{yx} = -\eta \left[ \frac{\partial u_y}{\partial x} + \frac{\partial u_x}{\partial y} \right] \quad (49)$$

and

$$C_y^{(1)} = -\frac{\partial P_{xy}^{(C)}}{\partial x} = \eta^{(C)} \frac{\partial^2 u_y}{\partial x^2} \quad (50)$$

in order to establish a relation between the macroscopic  $\eta$  coefficient and the microscopic level represented by  $C_i^{(1)}$ .

Using eq. (46) and expanding to second order in  $\sigma$  we obtain

$$C_y^{(1)}(\mathbf{r}, t) = mv_T^2 \sigma^4 g_2(\sigma) n_0^2 \frac{1}{\sqrt{\pi} v_T} \frac{\partial^2 u_y}{\partial x^2} \int d^{d+1} \hat{\sigma} \hat{\sigma}_y^2 \hat{\sigma}_x^2 = mv_T \sigma^4 g_2(\sigma) n_0^2 \frac{1}{\sqrt{\pi}} \frac{\partial^2 u_y}{\partial x^2} \frac{4\pi}{15} \quad (51)$$

where  $g_2(\sigma)$  is the radial distribution function at contact. By comparing (51) and (50) we obtain

$$\eta^{(C)} = \frac{4}{15} mv_T \sqrt{\pi} \sigma^4 g_2(\sigma) n_0^2 = 0.266 \sqrt{k_B T \pi m} g_2(\sigma) n_0^2 \sigma^4 \quad (52)$$

which is the viscosity found by Longuet-Higgins and Pople<sup>27</sup> the case of hard-spheres, whereas Enskog formula<sup>28</sup> at high density gives  $\eta_{Enskog}^{(C)} = 0.337 \sqrt{k_B T \pi m} g_2(\sigma) n_0^2 \sigma^4$ .

*Bulk viscosity.* Similarly if one assumes  $\mathbf{u} = (u_x(x, 0), 0, 0)$ , recalls  $C_x^{(1)}(\mathbf{r}, t) = -\frac{\partial P_{xx}}{\partial x}$  and uses the macroscopic relation

$$\frac{\partial P_{xx}}{\partial x} = -(\eta_b + \frac{4}{3}\eta) \frac{\partial^2 u_x}{\partial x^2}$$

can extract the bulk viscosity. Expanding  $C_x^{(1)}$  to second order in  $\sigma$  we find

$$C_x^{(1)}(\mathbf{r}, t) = mv_T^2 \sigma^4 g_2(\sigma) n_0^2 \frac{1}{\sqrt{\pi} v_T} \frac{\partial^2 u_x}{\partial x^2} \int d^4 \hat{\sigma} \hat{\sigma}_x^4 = mv_T \sigma^4 g_2(\sigma) n_0^2 \frac{1}{\sqrt{\pi}} \frac{\partial^2 u_x}{\partial x^2} \frac{4\pi}{5} \quad (53)$$

That is  $\eta_b^{(C)} = \frac{5}{3}\eta^{(C)}$ .

*Thermal conductivity.* The thermal conductivity can be computed assuming that both the density and the velocity are uniform throughout the system, i.e.  $n(\mathbf{r}, t) = n_0$  and  $\mathbf{u}(\mathbf{r}, t) = 0$ . In this case the heat flux is proportional to the temperature gradient:  $\mathbf{q}^{(C)}(\mathbf{r}, t) = -\lambda^{(C)} \nabla T(\mathbf{r}, t)$  and  $C^{(2)}(\mathbf{r}, t) = -\nabla \cdot \mathbf{q}^{(C)}(\mathbf{r}, t)$ . We assume a temperature profile varying only along the x-direction  $T(x, t)$  and use eq.(47), so that after some simple calculations and expanding to second order in  $\sigma$  we obtain

$$C^{(2)}(\mathbf{r}, t) = mv_T^3 g_2(\sigma) n_0^2 \sigma^4 \frac{1}{\sqrt{\pi}} \frac{k_B}{mv_T^2} \frac{1}{2} \nabla^2 T(\mathbf{r}, t) \int d^{d-1} \hat{\sigma} \hat{\sigma}_x^2 = mv_T \sigma^4 g_2(\sigma) n_0^2 \frac{k_B}{m} \frac{2\sqrt{\pi}}{3} \nabla^2 T(\mathbf{r}, t) \quad (54)$$

The heat conductivity HS excess is

$$\lambda^{(C)} = \frac{2}{3} \sqrt{k_B T \pi m} g_2(\sigma) n_0^2 \sigma^4 \frac{k_B}{m} = 0.666 \sqrt{k_B T \pi m} g_2(\sigma) n_0^2 \sigma^4 \frac{k_B}{m} \quad (55)$$

while Enskog formula at high density gives  $\lambda_{Enskog}^{(C)} = 1.269 \sqrt{k_B T \pi m} g_2(\sigma) n_0^2 \sigma^4 \frac{k_B}{m}$

#### D. Beyond hard core dynamics

In the case of more realistic potentials, such as the Lennard-Jones interaction, a satisfactory theory for dense systems is still missing. The situation has been reviewed recently by Stell and coworkers<sup>29</sup>. They compared different theories of transport in the Lennard-Jones fluid. These include a kinetic variational theory (KVT)<sup>30</sup>, and a stochastic approach put forward in its original form by Leegwater<sup>31</sup> and later reformulated by Polewczak and Stell<sup>32</sup> which introduces a random distribution of diameters of hard-spheres in the collision term.

The KVT applies to Lennard-Jones (LJ) fluids and is obtained by adding a hard-sphere core to the attractive tail of the LJ potential. The transport coefficients exhibit Enskog-like forms, but the radial distribution function bears explicit dependence on the LJ tail as

well as on the hard-sphere core. The hard sphere diameter is determined according to the well-known WCA method used in equilibrium statistical mechanics to mimic the LJ fluid<sup>33</sup>.

We shall not try to apply these theories in the present paper, a task beyond our scope, although the stochastic method could perhaps be implemented in our scheme. We shall only comment that the difficulty for continuous interactions is that there are not instantaneous collisions followed by free streaming trajectories as in the case of hard spheres. Instead, the collisions have a finite duration and a second collision event can take place before the first one is completed. A possible workaround could be to consider the motion of each particle as the combination of continuous momentum changes and almost instantaneous collisions. These small momentum changes represent the effect of weak attractive forces exerted by the surrounding molecules and can be assimilated to the random white noise forces occurring in the Brownian motion. In the literature, Rice and Allnatt combined the hard-core and the soft fluctuating potential model<sup>11,34</sup>. They represented the collisional term as a sum of the Enskog-Boltzmann collision integral, describing the large momentum binary exchanges plus a Fokker-Planck collision operator, supplemented by an average force, to model the small momentum exchanges due to the attractive forces, and assumed that these processes proceed without mutually interfering.

This separation should be feasible, since in many simple fluids the pair potential can be decomposed into the sum of a short range harsh repulsive potential contribution, plus a an attractive long range tail. The fine details of such a decomposition depend on the accuracy of the approximation, the most popular methods being the Weeks-Chandler-Andersen (WCA) and the Barker-Henderson<sup>35</sup> ones. It is therefore possible to treat the short range part with the technique employed in the case of the hard spheres and the tail of the interaction in the adiabatic approximation illustrated in section III. On the other hand, there are other possibilities. One of them consists in approximating the full continuous potential by a stepwise potential for which one can derive a proper extension of the RET equation, but the method seems exceedingly cumbersome to be of practical relevance.

In conclusion, as far as we are interested in studying systems of particles with realistic potentials we can treat the attractive tails in a mean field (Vlasov) fashion and the repulsion as if determined by a hard-spheres with a diameter suitably chosen. Since  $C_i^{(1)}$  and  $C^{(2)}$  do not have dependence on velocity and temperature gradients, they cannot contribute to the transport coefficients. To be more explicit, by projecting the interaction  $\Omega$  over the

hydrodynamic space, the resulting “matrix elements” do not depend on the fields  $\mathbf{u}$  and  $T$ , i.e. the Vlasov approximation only accounts for the distortion of the density  $n$  from its equilibrium value. Thus, the transport coefficients are only related to the BGK term and are purely kinetic within this approximation.

## V. SOLUTION BY LATTICE BOLTZMANN STRATEGY

The Lattice Boltzmann represents an alternative to methods which involve the direct solutions of coupled hydrodynamic equations of the type (7), (8) and (9). These equations represent projections of the evolution, eq.(33), and are not closed, since even the kinetic contributions of the pressure tensor and heat flux vector are not expressible solely in terms of the  $n$ ,  $\mathbf{u}$  and  $T$ . The necessary information to determine these contributions is contained in the higher moments of the distribution function. One can avoid the difficulty of computing these moments by using a macroscopic point of view which assumes constitutive relations, i.e. introduces phenomenological linear relations between  $P_{ij}$  and  $\mathbf{q}$  and the velocity and temperature, respectively. Alternatively, one is faced with the problem of closing a dynamical infinite hierarchy of equations. We instead propose to solve eq.(33) directly, with the only approximation stemming from the discretization procedure.

The LB method first evolved as empirical extension of lattice gas automata and found wide application as a standard simulation tool in computational fluid-dynamics<sup>37</sup>. In subsequent years, the LB method was found to be a systematic procedure to solve numerically a kinetic equation in velocity space<sup>39,40,41</sup>. Having in mind the simulation of condensed systems in micro/mesoscopic conditions, the critical parameter governing the departure from equilibrium is the Knudsen number,  $\epsilon$ , being the ratio between the mean free path and the representative length scale. On the nanoscale,  $\epsilon$  can be arbitrarily large and the numerical method should offer great flexibility with respect to external conditions and the Knudsen value.

As previously shown, a direct solution of eq. (1) is numerically very demanding in the case of a realistic form of the collision term  $\Omega(f)$  due to the large number of integrations over the phase-space variables. In this section we focus on the general strategy to solve the kinetic equation (33) in the adiabatic approximation, i.e. for  $C^{(2)} = 0$  and the system is rigorously isothermal. However, extending these concepts to the presence of heat transport is rather

straightforward, along the lines discussed below. Moreover, we assume that the functional  $g_2(\mathbf{r}, \mathbf{r}', t|n)$  is completely known by some level of theory or from atomistic simulations, such as Molecular Dynamics. In the study of fluids under non-equilibrium conditions, the proposed scheme has a strategic advantage over conventional atomistic simulations schemes since it exploits the pre-averaged nature of the kinetic description, avoiding the need to average observables over different realizations of the noise.

The starting point to derive a consistent numerical scheme is the representation for both the distribution function and the collisional terms over a finite set of Hermite polynomials. The distribution  $f(\mathbf{r}, \mathbf{v}, t)$  is approximated by

$$\bar{f}(\mathbf{r}, \mathbf{v}, t) = \omega(v) \sum_{l=0}^K \frac{1}{v_T^{2l} 2^l l!} \phi^{(l)}(\mathbf{r}, t) h^{(l)}(\mathbf{v}) \quad (56)$$

with  $\omega(v) = (2\pi v_T^2)^{-3/2} e^{-v^2/2v_T^2}$ . To keep the notation compact, in the following we use the convention that the product of tensors implicitly indicates the sum over all permutations of the tensorial indices. By construction, the complete and truncated distributions have the same coefficients up to Hermite order  $K$ , i.e.

$$\int d\mathbf{v} h^{(l)}(\mathbf{v}) f(\mathbf{r}, \mathbf{v}, t) = \int d\mathbf{v} h^{(l)}(\mathbf{v}) \bar{f}(\mathbf{r}, \mathbf{v}, t) \quad \text{for } l \leq K \quad (57)$$

Being the distribution coefficients  $\phi^{(l)}$  a combination of the distribution moments up to  $l$  order, the full and truncated distributions share the same moments up to  $K$  order.

Similarly, the collision operator is replaced by a truncated representation over the same Hermite set. We distinguish between the non-hydrodynamic relaxation term, taken here as the BGK relaxation (32), and the collisional term, renamed as  $\mathcal{K}(\mathbf{r}, \mathbf{v}, t) \equiv \frac{1}{m} C_i^{(1)}(\mathbf{r}, \mathbf{v}, t) \partial_{v_i} \Phi_M(\mathbf{r}, \mathbf{v}, t) \equiv \frac{1}{mn(\mathbf{r}, \mathbf{v}, t)} C_i^{(1)}(\mathbf{r}, \mathbf{v}, t) \partial_{v_i} f^{eq}(\mathbf{r}, \mathbf{v}, t)$ . Alternatively, the straight heat-bath operator (30) or momentum-preserving version (30) can be chosen and treated along similar lines<sup>43,44</sup>. In this way, the colloidal/density functional dynamics or a different microscopic dynamics for the non-hydrodynamic modes can be selected. The corresponding truncated representations are

$$\overline{\delta\Omega}(\mathbf{r}, \mathbf{v}, t) = \omega(v) \sum_{l=0}^K \frac{1}{v_T^{2l} 2^l l!} \psi^{(l)}(\mathbf{r}, t) h^{(l)}(\mathbf{v}) \quad (58)$$

and

$$\bar{\mathcal{K}}(\mathbf{r}, \mathbf{v}, t) = \omega(v) \sum_{l=0}^K \frac{1}{v_T^{2l} 2^l l!} \chi^{(l)}(\mathbf{r}, t) h^{(l)}(\mathbf{v}) \quad (59)$$

Again, each collisional term shares the same  $K$  moments with the original collisional counterpart.

The next step is to employ Gauss-Hermite quadratures to evaluate hydrodynamic and collisional moments. Recognizing that  $\bar{f}(\mathbf{r}, \mathbf{v}, t)h^{(l)}(\mathbf{v})/\omega(v) = p(\mathbf{r}, \mathbf{v}, t)$  is a polynomial in  $\mathbf{v}$  of degree  $\leq 2K$ , the moments can be evaluated exactly with quadratures of order  $2G \geq K$ , since

$$\begin{aligned}\phi^{(l)}(\mathbf{r}, t) &= \int d\mathbf{v} \bar{f}(\mathbf{r}, \mathbf{v}, t) h^{(l)}(\mathbf{v}) = \int d\mathbf{v} \omega(\mathbf{v}) p(\mathbf{r}, \mathbf{v}, t) \\ &= \sum_{p=0}^G w_p p(\mathbf{r}, \mathbf{c}_p, t) = \sum_{p=0}^G f_p(\mathbf{r}, t) h^{(l)}(\mathbf{c}_p)\end{aligned}\quad (60)$$

where  $f_p(\mathbf{r}, t) \equiv w_p \bar{f}(\mathbf{r}, \mathbf{c}_p, t)/\omega(c_p)$ , the vectors  $\mathbf{c}_p$  are a set of quadratures nodes and  $w_p$  the associated quadrature weights. Similarly, the collisional moments are computed as

$$\psi^{(l)}(\mathbf{r}, t) = \sum_{p=0}^G \delta\Omega_p(\mathbf{r}, t) h^{(l)}(\mathbf{c}_p) \quad (61)$$

$$\chi^{(l)}(\mathbf{r}, t) = \sum_{p=0}^G \mathcal{K}_p(\mathbf{r}, t) h^{(l)}(\mathbf{c}_p) \quad (62)$$

In summary, with the truncated Hermite representation and Gauss-Hermite quadratures, the distribution is replaced by an array of  $Q$  populations,  $f(\mathbf{r}, \mathbf{v}, t) \rightarrow f_p(\mathbf{r}, t) = w_p \bar{f}(\mathbf{r}, \mathbf{c}_p, t)/\omega(c_p)$  and similarly for the collisional term,  $\delta\Omega(\mathbf{r}, \mathbf{v}, t) \rightarrow \delta\Omega_p(\mathbf{r}, t) = w_p \bar{\delta\Omega}(\mathbf{r}, \mathbf{c}_p, t)/\omega(c_p)$  and  $\mathcal{K}(\mathbf{r}, \mathbf{v}, t) \rightarrow \mathcal{K}_p(\mathbf{r}, t) = w_p \bar{\mathcal{K}}(\mathbf{r}, \mathbf{c}_p, t)/\omega(c_p)$ . The nodes  $\mathbf{c}_p$  are chosen as vectors connecting neighboring mesh points  $\mathbf{r}$  on a lattice, mirroring the hop of particles between mesh points, generally augmented by a null vector  $\mathbf{c}_0$  accounting for particles at rest. The specific form of the lattice velocities and weights depends on the order of accuracy of the method and reflects the required Hermite order, as described in the following and thoroughly discussed in ref.<sup>42</sup>. The mesh is a Cartesian grid and the lattice velocities satisfy the sum rules,  $\sum_p w_p c_{pi} = 0$ ,  $\sum_p w_p c_{pi} c_{pj} = v_T^2 \delta_{ij}$ ,  $\sum_p w_p c_{pi} c_{pj} c_{pk} = 0$  and  $\sum_p w_p c_{pi} c_{pj} c_{pk} c_{pl} = v_T^4 (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk})$ , in order to guarantee mass and momentum conservation and isotropy.

The third step of the procedure is to propagate the distribution via a discretization of the streaming operator to first order, as a forward Euler update,

$$f_p(\mathbf{r} + \Delta t \mathbf{c}_p, t + \Delta t) = f_p(\mathbf{r}, t) + \Delta t w_p \sum_{l=0}^K \frac{1}{v_T^{2l} l!} [\psi^{(l)}(\mathbf{r}, t) + \chi^{(l)}(\mathbf{r}, t)] h^{(l)}(\mathbf{c}_p) \quad (63)$$

where  $\Delta t$  is the LB time-step. Consequently, the algorithm exploits the same Cartesian mesh to rearrange populations over spatial and velocity shifts.

The population dynamics is able to reproduce the target macroscopic evolutions, such as the Navier-Stokes equation, to high accuracy. In the appendix a formal Chapman-Enskog multiscale analysis shows that for a second-order of accuracy in the transport coefficients, a second order expansion in Hermite is needed for both the equilibrium distribution and the collisional integral. As a result, the final form of the LB algorithm reads

$$f_p(\mathbf{r} + \mathbf{c}_p, t + 1) = (1 - \frac{\Delta t}{\tau})f_p(\mathbf{r}, t) + \frac{\Delta t}{\tau}f_i^{eq}(\mathbf{r}, t) + \Delta t\mathcal{K}_i(\mathbf{r}, t) \quad (64)$$

where the relaxation time  $\tau$  is related to the kinetic component of the shear viscosity via

$$\eta^{(K)} = nv_T^2(\tau - \frac{\Delta t}{2}) \quad (65)$$

i.e. the physical value (compare with eq. (40)) minus a viscosity of numerical origin. Some straightforward algebra shows that the final form of the discrete equilibrium reads

$$f_p^{eq} = w_p n(\mathbf{r}, t) \left[ 1 + \frac{c_{pi}u_i(\mathbf{r}, t)}{v_T^2} + \frac{(c_{pi}c_{pj} - v_T^2\delta_{ij})u_i(\mathbf{r}, t)u_j(\mathbf{r}, t)}{2v_T^4} \right] \quad (66)$$

which is tantamount to a low-Mach ( $O[Ma^3]$ ) expansion of the local Maxwellian, while the discretized form of the collisional term is

$$\mathcal{K}_p = -w_p \frac{1}{m} \left[ \frac{c_{pi}C_i^{(1)}(\mathbf{r}, t)}{v_T^2} + \frac{(c_{pi}c_{pj} - v_T^2\delta_{ij})u_i(\mathbf{r}, t)C_j^{(1)}(\mathbf{r}, t)}{v_T^4} \right] \quad (67)$$

A popular mesh model that reproduces the second order Hermite accuracy is provided by the so-called D3Q19 model<sup>37</sup>, consisting of 19 discrete velocities in three dimensions, and with  $v_T = 1/\sqrt{3}$ .

A further issue concerns the calculation of the spatial convolution present in the collisional term. From the above discussion it is clear that the central issue in LB related methods is the discretization of velocity space with the ensuing level of accuracy in the macroscopic transport equations. On the other hand, the method is completely flexible in terms of the mesh spacing  $\Delta x$ , that can be tuned at will in order to resolve the details of the microscopic interactions. Therefore, the error introduced in the spatial discretization does not represent a critical issue. As an example, in a previous paper<sup>36</sup> we solved numerically eq. (33) by means of the Lattice Boltzmann method<sup>37</sup> using as a test case the flow of a hard-sphere fluid through a narrow channel with a pressure gradient along its axis, and measuring the

deviations from the macroscopic Poiseuille law. The spatial convolutions were evaluated with spatial quadratures over a number of off-mesh points obtained via linear interpolations, one of several alternatives to compute such integrals to desired level of accuracy.

Regarding the stability of the proposed method, it is worth mentioning that even for simple non-interacting dynamics the LB algorithm is subjected to numerical instability. By using a von Neumann linear stability analysis, it has been shown that a stable LB scheme requires that the flow velocity be below a certain threshold that is a function of the relaxation time and the wave number<sup>45</sup>. The action of stiff intermolecular forces clearly narrows the stability range. Nevertheless, a generic upper bound for the variation of populations due to the forcing term is  $\delta f/f \sim f_p/w_p \sim \Delta t \mathcal{K}_p \ll 1$ . Therefore, for a generic quadrature scheme, the convolution force is  $C^{(1)}/\Delta x^3 \sim n F g_2$ , and the forcing term should be  $n F g_2 \ll 1/\Delta x^4$  since  $\Delta x/\Delta t \sim 1$ , showing that the stability upper bound raises rapidly when reducing the mesh spacing.

## VI. CONCLUSIONS

To summarize, we have presented a theoretical analysis and proposed a computational scheme which bridge hydrodynamics with microscopic structural theories of fluids. The present approach shows that the dynamic density functional and Boltzmann-like methods can be derived in a unique framework. The differences between the two methods are determined by the interaction of the fluid with the heat bath. The DDF method applies to colloids which are embedded in a solvent whose degrees of freedom are represented by a viscous heat bath, not moving with the particles, which eliminates all the hydrodynamic modes, but the diffusive mode. Boltzmann methods, instead, apply to molecular fluids and the corresponding heat bath is determined by degrees of freedom internal to the fluids and therefore moves with the fluid.

A further improvement could concern the dependence of the hydrodynamic fields  $\mathbf{u}(\mathbf{r}, t)$  and  $T(\mathbf{r}, t)$  on the local distribution  $f(\mathbf{r}, \mathbf{v}, t)$ . One could expect that these fields should be obtained via a coarse-grained prescription starting from  $\phi_M(\mathbf{r}, \mathbf{v}, t)$  because the hydrodynamics cannot be extended beyond the size of few diameters. In fact, at scales shorter than a few molecular diameters hydrodynamic modes are strongly damped, with a decay time so short that the time autocorrelation function of a single molecule is isotropic. There-



fore, descriptions based on hydrodynamic field could become inappropriate at that scale<sup>46</sup>. This program has been carried on for the hard sphere model in ref.<sup>36</sup> by employing a radial distribution function constructed according to the prescription of Fischer and Methfessel<sup>47</sup>. It is assumed that  $g_2(\mathbf{r}, \mathbf{r}'|n)$  depends on a coarse-grained density  $\bar{n}(\mathbf{r}, t)$  via a uniform smearing over a sphere of radius  $\sigma/2$ . As a consequence the collisional terms (46) and (47) depend non locally not only from the density as in DDF but also from the temperature and velocity field.

In the final section of the paper we showed how the derived kinetic equations can be transformed into a numerical scheme by following the theoretical derivation, i.e. by relying on a truncated Hermite representation of the collisional integrals and the unknown distribution, complemented by Gauss-Hermite quadratures to evaluate the distribution moments. Previous implementations of these ideas by us have proved that this numerical approach can be successfully applied to the study of inhomogeneous fluids.

## VII. ACKNOWLEDGMENTS

UMBM thanks Pedro Tarazona for correspondence.

## APPENDIX A: CHAPMAN-ENSKOG ANALYSIS

Let us analyze the multi-scale dynamics in powers of the Knudsen number  $\epsilon$ , with the distribution expanded as

$$f = f^{eq} + \epsilon f^{(1)} + \epsilon^2 f^{(2)} + \dots \quad (\text{A1})$$

The dynamics is further decomposed based on the intrinsic hierarchy of timescales. For example, one can distinguish between the short-time convective motion, over a spatial scale  $x \rightarrow \epsilon x$  and temporal scale  $t_1 = \epsilon t$ , and the slower evolution set by momentum diffusion,  $t_2 = \epsilon^2 t$ . Expressing the derivatives as

$$\partial_t = \epsilon \partial_t^{(1)} + \epsilon^2 \partial_t^{(2)} + \dots \quad (\text{A2})$$

$$\partial = \epsilon \partial \quad (\text{A3})$$

the Lattice Boltzmann streaming step is expressed as

$$f_p(\mathbf{r} + \mathbf{c}_p, t + 1) - f_p(\mathbf{r}, t) = (\epsilon \partial_t^{(1)} + \epsilon^2 \partial_t^{(2)} + \dots + \epsilon c_p \partial)(f_p^{eq} + \epsilon f_p^{(1)} + \dots)$$

having set  $\Delta t = 1$ . We now employ the explicit form of the kinetic equation (33). The collision operator has an intrinsic dependence on  $\epsilon$ , and the BGK term reads

$$\frac{1}{\tau}(f_p^{eq} - f_p) = -\frac{1}{\tau}(\epsilon f_p^{(1)} + \epsilon^2 f_p^{(2)} + \dots) \quad (\text{A4})$$

where, as shown next, the relaxational time  $\tau$  is related to the kinetic component of the shear viscosity. The collisional term in (33) is a non-linear functional of the density, multiplied by  $\partial_v f^{eq}$ , that depends on density and momentum density, so that the fastest evolution is on the  $\epsilon$  scale,

$$\mathcal{K} = \epsilon \mathcal{K}^{(1)} + \epsilon^2 \mathcal{K}^{(2)} + \dots \quad (\text{A5})$$

and  $\mathcal{K}^{(0)} = 0$ . By equating the same orders in  $\epsilon$ , the evolutions on the  $\epsilon$  scale is

$$(\partial_t^{(1)} + c_p \partial) f_p^{eq} = -\frac{f_p^{(1)}}{\tau} + \mathcal{K}_p^{(1)} \quad (\text{A6})$$

and on  $\epsilon^2$  scale

$$\begin{aligned} & \partial_t^{(1)} f_p^{(1)} + \partial_t^{(2)} f_p^{eq} + \partial_{c_p} f_p^{(1)} + \frac{1}{2} c_p c_p \partial^2 f_p^{eq} + \partial \partial_t^{(1)} c_p f_p^{eq} + \frac{1}{2} \partial_t^{(1)} \partial_t^{(1)} f_p^{eq} \\ &= -\frac{f_p^{(2)}}{\tau} + \mathcal{K}_p^{(2)} \end{aligned} \quad (\text{A7})$$

Substituting eq.(A6) into the fourth and last terms in the l.h.s. of eq.(A7), and by rearranging terms, the  $\epsilon^2$  dynamics can be rewritten as

$$\left( \partial_t^{(1)} + c_p \partial \right) \left[ \left( 1 - \frac{1}{2\tau} \right) f_p^{(1)} + \frac{1}{2} \mathcal{K}_p^{(1)} \right] + \partial_t^{(2)} f_p^{eq} = -\frac{f_p^{(2)}}{\tau} + \mathcal{K}_p^{(2)} \quad (\text{A8})$$

Up to the momentum diffusivity scale, therefore, the evolution of the density and current are obtained by contracting the above equations as  $\sum_p(\cdot)$  and  $\sum_p \mathbf{c}_p(\cdot)$ , obtaining

$$\partial_t^{(1)} n + \partial_i^{(1)} (n u_i) = 0 \quad (\text{A9})$$

$$\partial_t^{(2)} n = 0 \quad (\text{A10})$$

$$\partial_t^{(1)} (n u_i) + \partial_j \left( n v_T^2 \delta_{ij} + n u_i u_j + P_{ij}^{(C,1)} \right) = 0 \quad (\text{A11})$$

$$\partial_t^{(2)} (n u_i) + \frac{1}{\epsilon} \partial_j \left( \left( 1 - \frac{1}{2\tau} \right) P_{ij}^{(K,neq)} + P_{ij}^{(C,2)} \right) = 0 \quad (\text{A12})$$

where  $P_{ij}^{(C,1)}$  and  $P_{ij}^{(C,2)}$  are the collisional contributions to the pressure tensor at first and second Knudsen order, respectively. In addition, some lengthy algebra shows that  $P_{ij}^{(K,neq)}$  is identified as the non-equilibrium part of the kinetic pressure tensor

$$P_{ij}^{(K,neq)} = \left( 1 - \frac{1}{2\tau} \right) \sum_p c_{pi} c_{pj} (f_p - f_p^{eq}) = \eta^{(K)} [\partial_i u_j + \partial_j u_i] \quad (\text{A13})$$

By multiplying eqs. (A9) and (A10) by  $\epsilon$  and eqs. (A11) and (A12) by  $\epsilon^2$  and summing the equations, we reconstruct the sought evolution for density and momentum density accurate to  $\epsilon^2$  level

$$\begin{aligned}\partial_t n + \partial_i(nu_i) &= 0 \\ \partial_t(nu_i) + \partial_j \left( nv_T^2 \delta_{ij} + P_{ij}^{(K)} + P_{ij}^{(C)} \right) &= 0\end{aligned}$$

At higher Knudsen order, the following recurrence relation holds<sup>42</sup>

$$f_p^{(k+1)} = -\tau \left[ \sum_{m=0}^k \partial_t^{(k)} f_p^{(m)} + c_p \partial f_p^{(k)} - \mathcal{K}_p^{(k+1)} \right] \quad (\text{A14})$$

where  $f^{(0)} \equiv f^{eq}$ . Similarly, for the Hermite coefficients,

$$\phi^{(n,k+1)} = -\tau \left[ \sum_{m=0}^k \partial_t^{(k)} \phi^{(n,m)} + n \partial \phi^{(n-1,k)} + \partial \phi^{(n+1,k)} - \chi^{(n,k+1)} \right] \quad (\text{A15})$$

where the first superscript of the coefficients refers to the Hermite truncation level and the second to the Knudsen level. If we neglect the collisional term, eq. (A15) shows that the dynamics of the coefficient  $\phi^{(n,k+1)}$  depends on  $\phi^{(n-1,k)}$ ,  $\phi^{(n+1,k)}$  and  $\phi^{(n,0)}$ , ...,  $\phi^{(n,k)}$  in a hierarchical (pyramidal) way. In order to guarantee a given level of accuracy on the Knudsen level, without introducing any approximation from the Hermite truncation, a complete representation is required on the base of the pyramid corresponding to the equilibrium distribution. In particular, for Knudsen order  $k$ , the equilibrium needs to include at least  $n + k + 1$  Hermite coefficients<sup>42</sup>. At first order in Knudsen, the equilibrium distribution should be accurate up to third Hermite order, complemented by fifth order quadratures to evaluate the moments. In order to handle thermal dynamics (in the presence of a non-zero heat flux), a fourth order accuracy in the equilibrium is required, together with seventh order quadratures.

When the collisional term is included, the simple hierarchical picture seems to be spoiled. However, by using the explicit Hermite representation of the collisional term, the third order Hermite coefficient  $\chi^{(3)} \sim u^3$ , a contribution that can be neglected in standard condensed matter conditions. If one retains only up to second order in  $f_p^{(eq)}$ , the error can be estimated, as discussed in<sup>42</sup>, to be  $\sim \frac{1}{\nu_0} u^2 \partial_x u$  in the pressure tensor and  $\sim u^2$  in the shear viscosity.

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